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Occurrence of preservatives and antimicrobials in Japanese rivers

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HIGHLIGHTS

- Seven preservatives and 5 antimicrobials were simultaneously analyzed in river water.
- Concentration of 2-phenoxyethanol, a cosmetic preservative, was high in rivers.
- Isopropylmethylphenol, resorcinol, and triclosan were detected ubiquitously.
- The ratio of methyl- to propyl-parabens was similar to that in cosmetic products.

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ABSTRACT

We established a method for the simultaneous analysis of seven preservatives and five antimicrobials in water. These chemicals are widely used in cosmetics, and their presence in river water is of concern. We used the method to test 13 sites in Japanese rivers and streams contaminated by domestic wastewater, effluent, or industrial wastewater. 2-Phenoxyethanol (2-PE), isopropylmethylphenol, resorcinol, and triclosan were detected at most sites; the maximum concentration of 2-PE detected was 14000 ng L⁻¹. The results suggest that the major sources of 2-PE were cosmetics and household detergents. The ratio of methylparaben to *n*-propylparaben in river waters with direct wastewater drainage was similar to that in common cosmetics. This is the first research on levels of 2-PE, isopropylmethylphenol, and chlorphenesin in river water.

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1. Introduction

Preservatives and antimicrobials are used in a wide range of soaps, toothpastes, cosmetics, hair styling products, sunscreens, and other daily personal care products (PCPs). Most are used to suppress microorganism growth in products. PCPs thus enter waters from households. Some of the components are not efficiently removed by wastewater treatment (McAvoy et al., 2002; Nakada et al., 2007; Kasprzyk-Hordern et al., 2009), and in unsewered areas, they enter waterways without appropriate treatment. Components of PCPs are among the most commonly detected

compounds in surface waters throughout the world (Kolpin et al., 2002; Moldovan, 2006; Kasprzyk-Hordern et al., 2008). Triclosan (TCS) can induce the expression of resistance and cross-resistance mechanisms in bacteria (Orvos et al., 2002; Tatarazako et al., 2004; Dussalt et al., 2008). Its occurrence in surface waters and wastewaters has been extensively studied (Kolpin et al., 2002; McAvoy et al., 2002; Loraine and Pettigrove, 2006; Cuderman and Heath, 2007; Trenholm et al., 2008; Kasprzyk-Hordern et al., 2009; Pedrouzo et al., 2009). Some reported concentrations in widely separated regions are high enough to trigger bacterial resistance in the environment also (SCCS, 2010). Furthermore, TCS has been detected in drinking water (Loraine and Pettigrove, 2006).

However, other preservatives or antimicrobials have not been thoroughly studied. Those used in large quantities in cosmetics are regulated in Japan (Ministry of Health and Welfare Notification of Japan, 2000). The standard for preservatives and antimicrobials

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in cosmetics lists about 50 ingredients, including 2-phenoxyethanol (ethylene glycol monophenyl ether: 2-PE) and parabens in lotions, resorcinol (1,3-benzenediol: RC) in hair dyes, TCS in hand soap, and isopropylmethylphenol (4-isopropyl-3-methylphenol: IPMP) in toothpaste and hand soap. 2-PE and RC are also included in the Organisation for Economic Co-operation and Development's (OECD) list of high-production-volume chemicals.

In recent years, 2-PE, a preservative, has been extensively used as a substitute for or in combination with parabens in cosmetics in Japan. Parabens are still used widely in cosmetics and foods. IPMP has come to be used in hand soaps and toothpastes as a substitute for TCS, which was shown to be toxic to aquatic organisms (SCCS, 2010). 2-PE, parabens, and benzoic acid are used most frequently, followed by chlorphenesin (CP), dehydroacetic acid, sorbic acid, and chloroxylenol (4-chloro-3,5-xylene: PCMX) as antibacterial agents in cosmetics (Mori et al., 2007). CP and dehydroacetic acid are used in skin lotions and creams for the treatment of acne; sorbic acid in foundations; and PCMX in deodorants, baby powders and creams. However, little information is available on their occurrence and ecotoxicity in water, as their analyses depend on specific methods. The objective of this study was to establish an analytical method to simultaneously measure a number of preservatives and antimicrobials in surface waters, and to obtain analytical data on their occurrence in the environment.

We present a method for the simultaneous determination of commonly used preservatives and antimicrobials in surface waters, and tested 13 sites in Japanese rivers contaminated by domestic wastewater, sewage treatment plant (STP) effluent, or industrial wastewater.

2. Materials and methods

2.1. Reagents and standards

The method covers seven preservatives and five antimicrobials (Table 1). 2-PE (>98.5% purity), methylparaben (MeP) (>99.0%), IPMP (>99.0%), RC (>99.0%), and PCMX (>98.0%) came from Wako Pure Chemical Industries, Japan. Ethylparaben (EtP) (>98.5%), *n*-propylparaben (*n*-PrP) (>98.5%), isopropylparaben (*i*-PrP) (>98.5%), *n*-butylparaben (*n*-BuP) (>98.5%), and isobutylparaben (*i*-BuP) (>98.5%) came from Kanto Chemical Co., Japan. CP (>98.5%) came from Alfa Aesar GmbH & Co. KG, Germany. TCS (>96.0%) came from Tokyo Chemical Industry, Japan. RC-2,4,5,6-*d*₄, TCS-*d*₃ (Toronto Research Chemicals Inc.), 2-PE-*d*₄, MeP-*d*₄, and *n*-PrP-*d*₄ (C/D/N Isotopes) were used as surrogates. The derivatizing reagent *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) came from Thermo Fisher Scientific Inc., USA.

2.2. Sample collection

River water samples were collected from four sites in Tokushima (T-1-4), four in Kyoto (K-1-4), and five in Saitama (S-1-5) (Fig. 1) during autumn 2010 and winter 2011. The Tokushima sites were small urban streams in an unsewered area; only T-1 was downstream of a community scale STP which served a small residential area. K-1 was a point on a river which flows through an area where 80% of the population is served with sewerage. Approximately 40% of total surface water at K-2 is sewage effluent. Almost all of the river water at K-3 consisted of treated wastewater. The water at K-4 contains wastewater from a hospital and residential aerobic septic tanks. All sites in Saitama were contaminated with industrial and domestic wastewater. Up to 80% of the population is served with sewerage. S-5 was located on a stream that flows through an area of low service coverage with many farms upstream. S-4 was sampled only in autumn and S-5 in winter.

2.3. Sample extraction

The samples were kept in cooled boxes and transported to the laboratory, where they were filtered through glass fiber filters (GF/C, Whatman) as soon as possible. The time elapsed between sampling in the field and filtering in the laboratory ranged from several hours and to 48 h. The particulate phase was not analyzed. The samples (1000 mL) were spiked with 200 ng of surrogates (RC-*d*₄, TCS-*d*₃, 2-PE-*d*₄, MeP-*d*₄, and *n*-PrP-*d*₄). They were then extracted by solid-phase extraction through tandem cartridges: Oasis HLB Plus type 225 mg (Waters Corp.) and InertSep SlimJ Pharma FF 230 mg (GL Sciences Inc.). The recovery of RC by the Oasis HLB was poor, but that by the InertSep SlimJ Pharma was sufficient. Both cartridges were conditioned first with ethyl acetate, methanol, and ultrapure water. The samples were passed through the cartridges at 10 mL min⁻¹. After sample loading, the cartridges were separated and the water in them was removed by syringe and centrifugation. Each cartridge was backflush-eluted with 8 mL ethyl acetate at 1 mL min⁻¹ using a Sep-Pak Elution pump (Waters Corp.). Both extracts were mixed and the water phase was removed with a Pasteur pipette. The solvent phase was reduced under a gentle stream of nitrogen at 40 °C until close to dryness, and the residue was then redissolved in 100 µL dichloromethane. The extracts were not cleaned up further, because some of the matrix was left in the green to brown aqueous phase.

As procedural blanks revealed small amounts of 2-PE and MeP, the concentrations were corrected by the blanks. Special care was taken to minimize sample contamination. All glassware was rinsed several times with acetone and ethyl acetate just before usage.

2.4. BSTFA derivatization

Derivatization of hydroxylated chemicals is advantageous for gas chromatography–mass spectrometry (GC–MS) analysis. The extracts dissolved in 100 µL dichloromethane were derivatized with 100 µL BSTFA at 40 °C for 1 h to increase the sensitivity and limits of detection of the hydroxylated target compounds.

2.5. Instrumental analysis

Chemical analysis was performed by GC (Trace GC) interfaced with an ion trap MS (Polaris-Q; Thermo Fisher Scientific Inc.) equipped with a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d., Agilent Inc.). The carrier gas was helium at a constant flow of 1.0 mL min⁻¹. The injector was operated in splitless mode (250 °C), and the injection volume was 2 µL. The oven temperature program started at 50 °C (held for 1 min), ramped at 20 °C min⁻¹ to 80 °C (held for 3 min), then increased at 20 °C min⁻¹ to 100 °C (held for 3 min), then at 10 °C min⁻¹ to 180 °C (held for 3 min), then 10 °C min⁻¹ to 300 °C (held for 10 min). The transfer line temperature was at 280 °C. The MS was operated in electron ionization mode with an energy of 70 eV. The ion source temperature was 250 °C. The mass range was 50–540 *m/z* in full-scan mode. A representative total ion chromatogram of a standard mixture is shown in Fig. 2. The quantifying ion, confirmatory ion, and surrogate for each analyte are shown in the supporting information (Table S1).

3. Results and discussion

3.1. Procedural recoveries

Reproducibility was examined with five replicate analyses of 1000 mL of ultrapure water spiked with 4 ng of standard chemicals. The quantity was set so that the final concentration before analysis should be the lowest on the calibration curves (20 µg L⁻¹).

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